Microphysical Modeling in GMI, Chemistry and Future Directions

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Outline

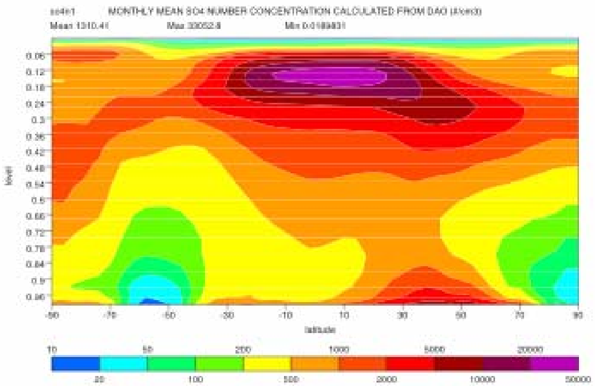
- Update on adding aerosol dynamics to GMI
- Prediction of nitrate and ammonium in IMPACT
- Future directions: Secondary organics

UMaer aerosol dynamics model added to GMI

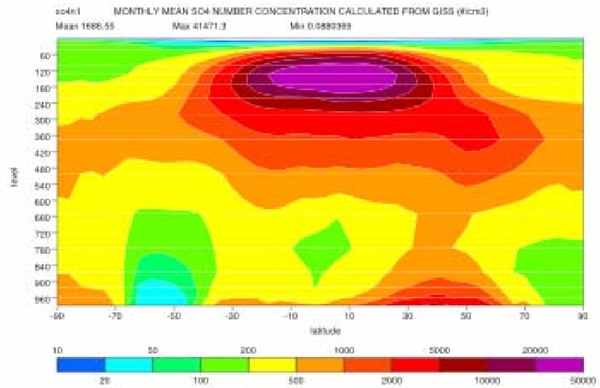
- UMaer: model of modes and moments
  - superposition of lognormal distributions with constant width
  - 2 moments: mass and number concentration
  - 4 nucleation schemes: Here use (Vehkamaki et al. 2002)
  - Treatment of coagulation with non-sulfate aerosol
  - Precipitation scavenging efficiency depends on SO_4 coverage

SO_4 number in bin 1 (# / cm^3)

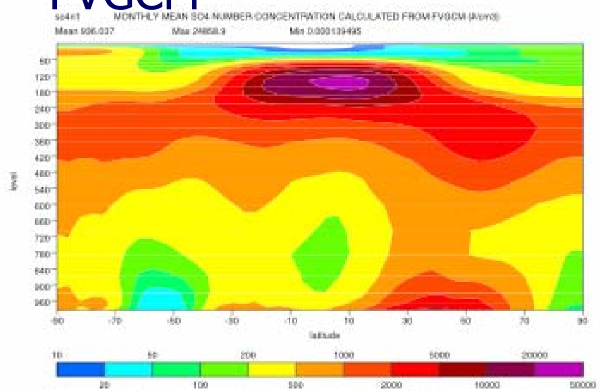
DAO

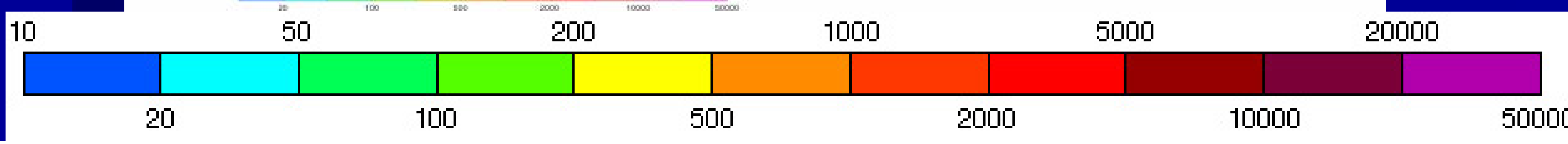


GISS

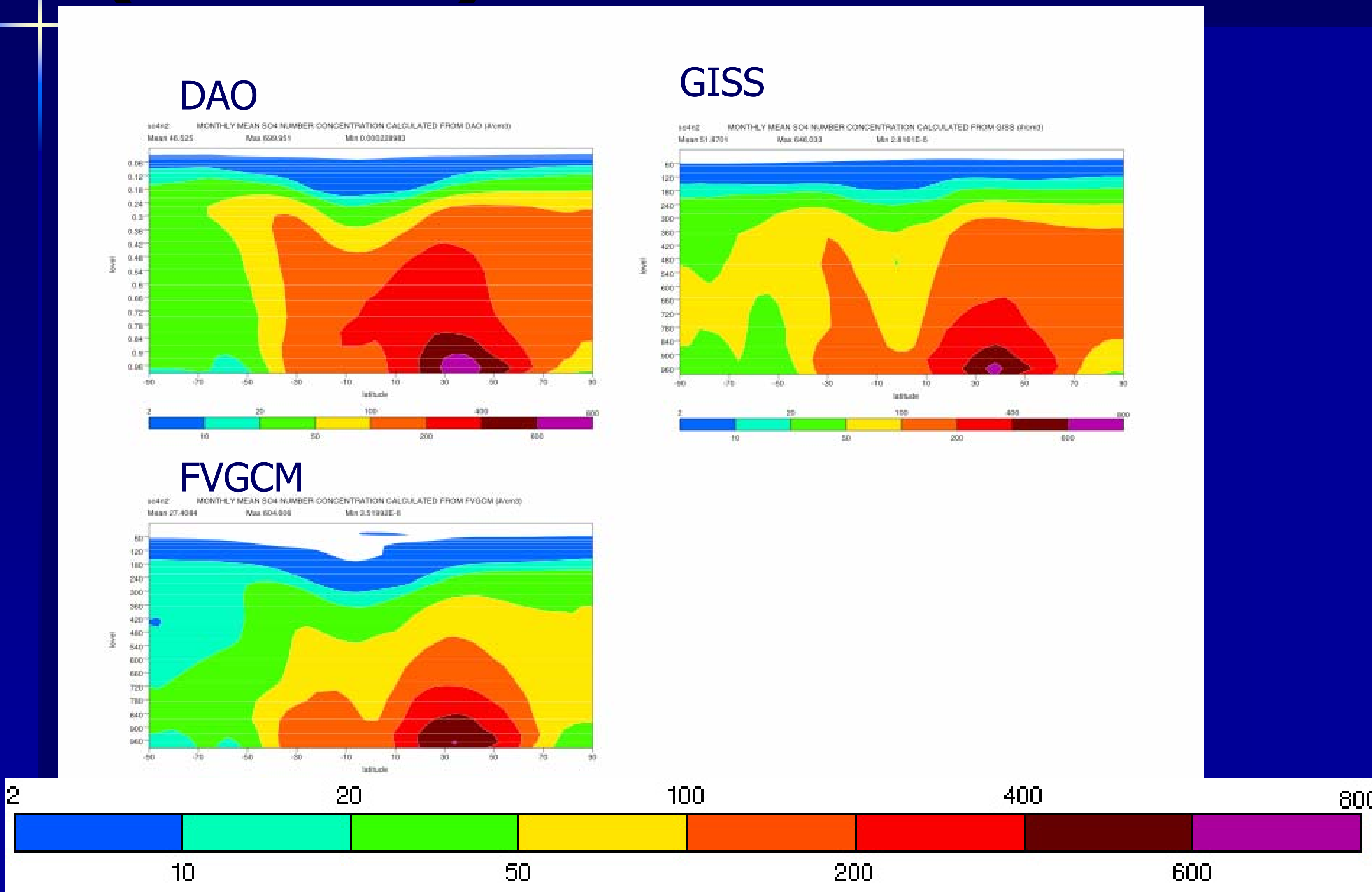


FVGCM



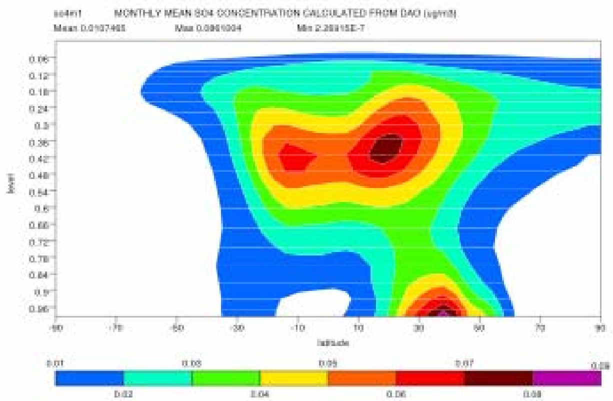


SO_4 number in bin 2 (# / cm^3)

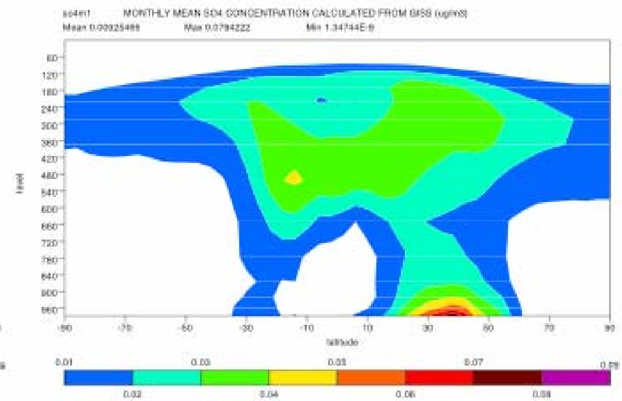


SO_4 mass in bin 1 ($\mu m/m^3$)

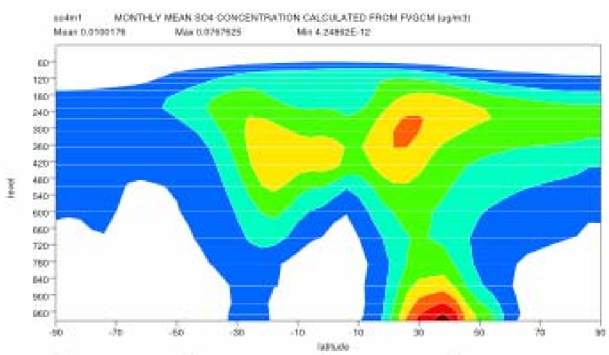
DAO



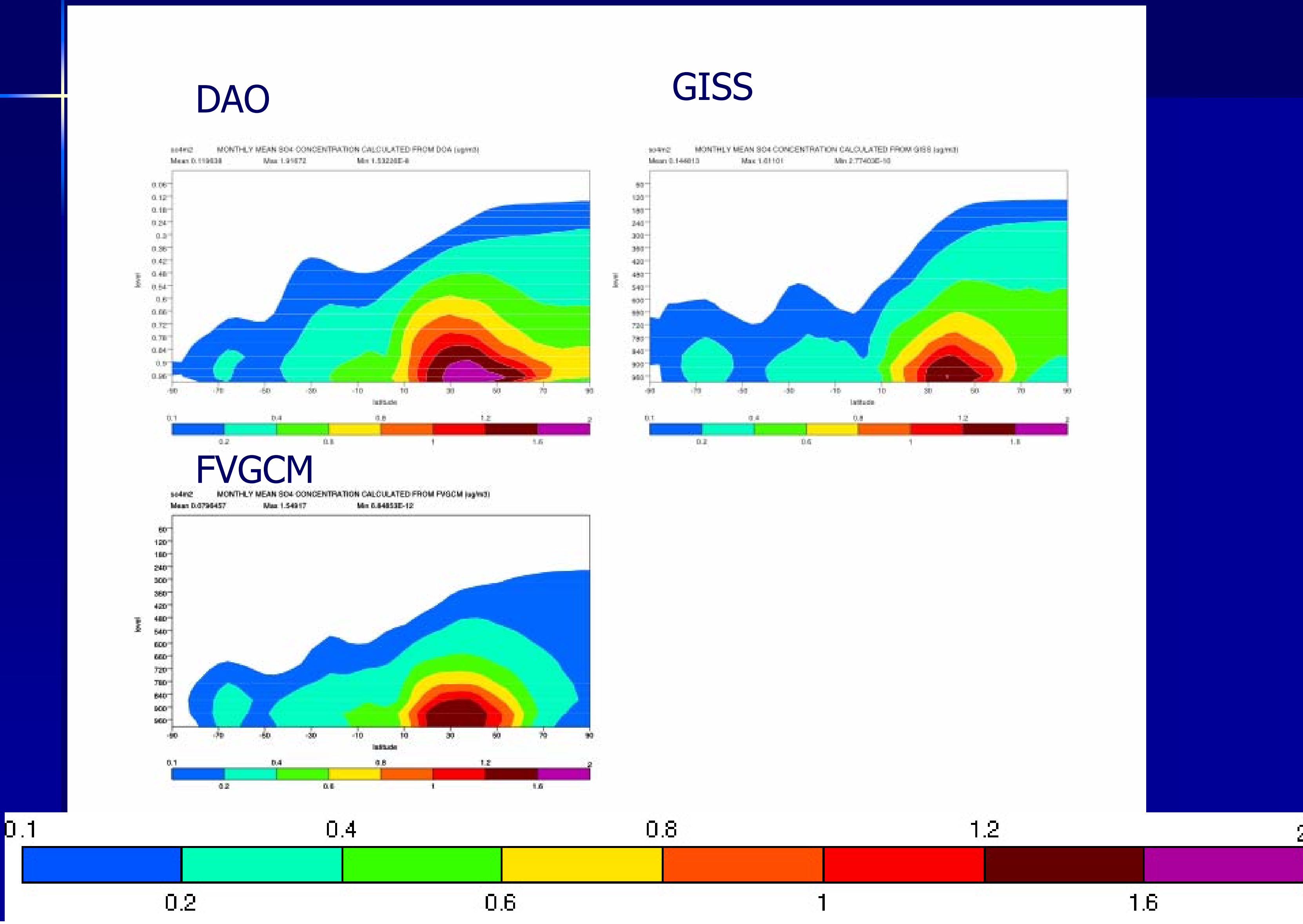
GISS



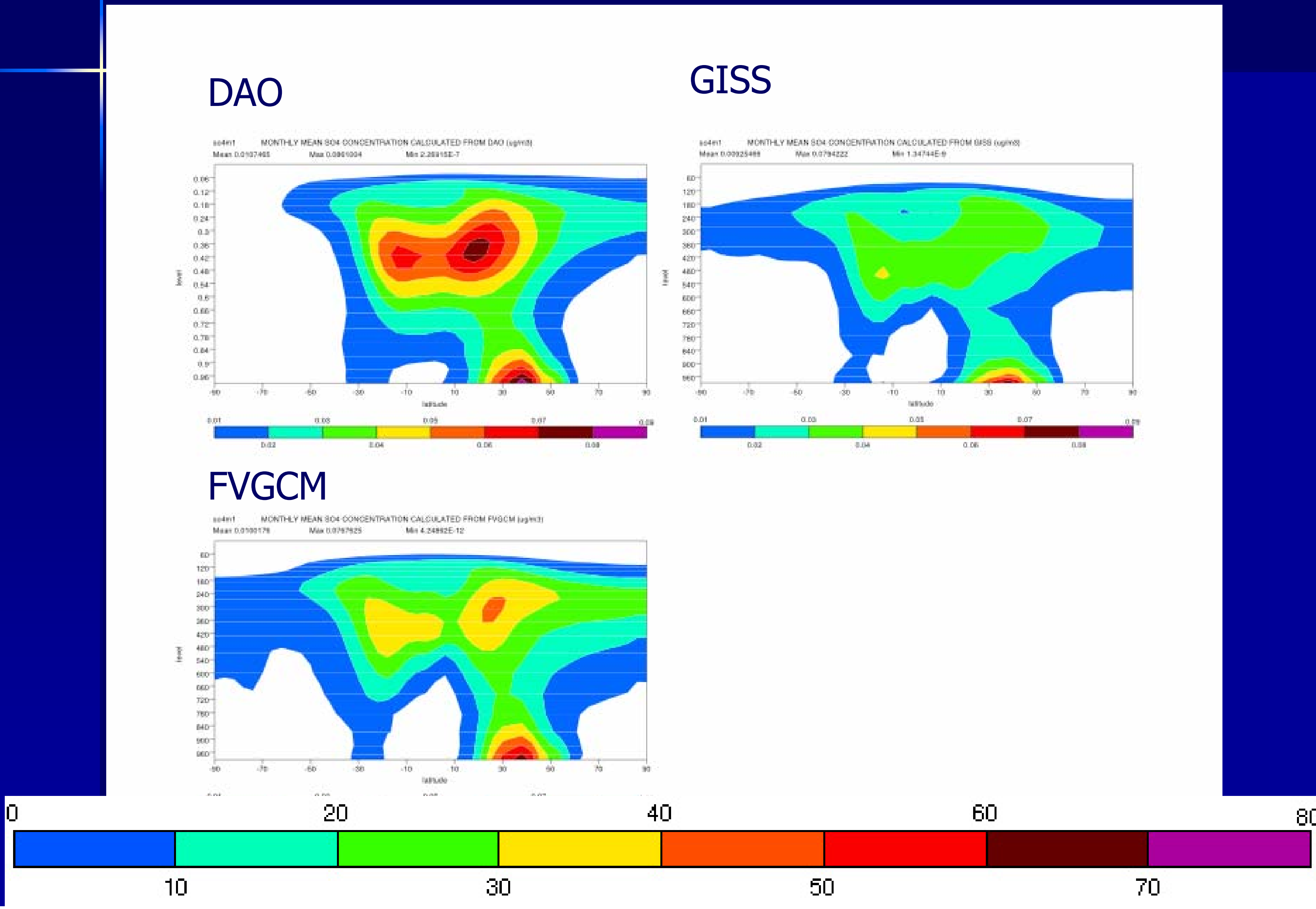
FVGCM



SO_4 mass in bin 2 ($\mu m / m^3$)



Fraction of SO_4 on non-sulfate aerosols (%)



Next steps ?? Possible choices:

- Write paper describing current differences
- Add Debra's method and compare results
- Examine differences in indirect forcing, then write paper
- Calculate direct forcing, then paper
  - Develop parameterization for internal mixtures with dust/sea salt

Global Modeling of Nitrate and Ammonium: Heterogeneous Interactions of Aerosol and Tropospheric Chemistry

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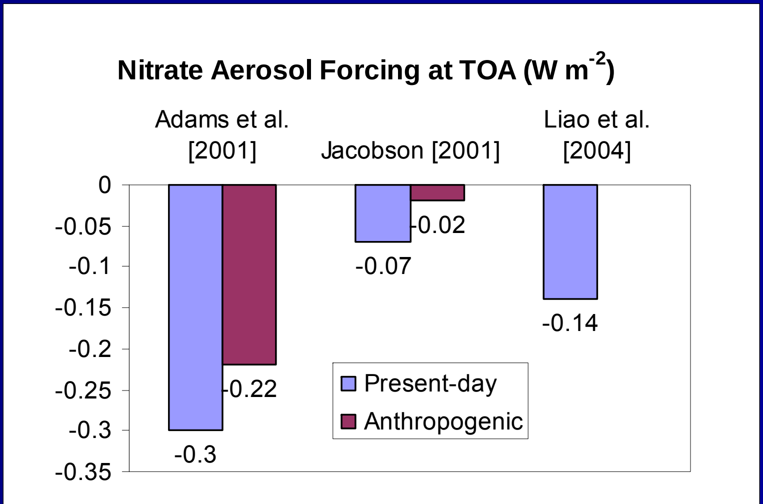
Nitrate and Ammonium are two Significant Sources of Anthropogenic Aerosol

- Direct radiative forcing by scattering;
- Condensation of nitric acid enhances aerosol activation to cloud droplets (e.g., *Kulmala et al.*, 1993, 1995, and 1998);
- The formation of nitrate aerosol lowers reaction probability of N_2O_5(g) conversion to HNO_3(g):



Tropospheric O_3 production $\longleftarrow NO_x \longleftrightarrow N_2O_5 + H_2O \longrightarrow 2NO_3^- + 2H^+ \longleftrightarrow HNO_3(g)$

Nitrate and Ammonium Aerosol Formation

- EQ: Thermodynamic equilibrium between the gas phase and aerosols (e.g., *Adams et al.,* 1999 and 2001; *Jacobson*, 2001);

- Bulk-aerosol phase establishes equilibrium with the gas phase, and nitrate and ammonium aerosol concentrations are distributed to different size sections by a weighting function derived from mass transfer equations (e.g., *Pandis et al.,* 1993; *Lurmann et al.,* 1997; *Rodriguez and Dabdub*, 2004);

- UPTAKE: the first-order removal rate based on HNO_3 uptake (reaction) coefficient is considered for the uptake of nitrate by aerosol (e.g., *Dentener and Crutzen*, 1993; *Dentener et al.,* 1996);

- HYB: use EQ for nitrate and ammonium on sulfate (and sea salt) aerosol, and use UPTAKE for nitrate on dust aerosol (*Liao et al.,* 2003 and 2004).

- DYN: use EQ for fine-mode (D≤1.25μm) nitrate and ammonium aerosol, and solves mass transfer equations for coarse-mode (D≥1.25μm, 3 size bins) nitrate and ammonium aerosol (*Capaldo et al.*, 2000):

$$
\begin{cases}
\dfrac{dC_\infty}{dt} = -\sum_i^n k_i (C_\infty - C_{i,eq}) \\
\dfrac{dC_i}{dt} = k_i (C_\infty - C_{i,eq}) \\
k_i = 4\pi D_g r_i n_i \dfrac{0.75\alpha(1+Kn_i)}{Kn_i^2 + Kn_i + 0.283 Kn_i \alpha + 0.75\alpha}
\end{cases}
$$

← C_∞ : gas concentration

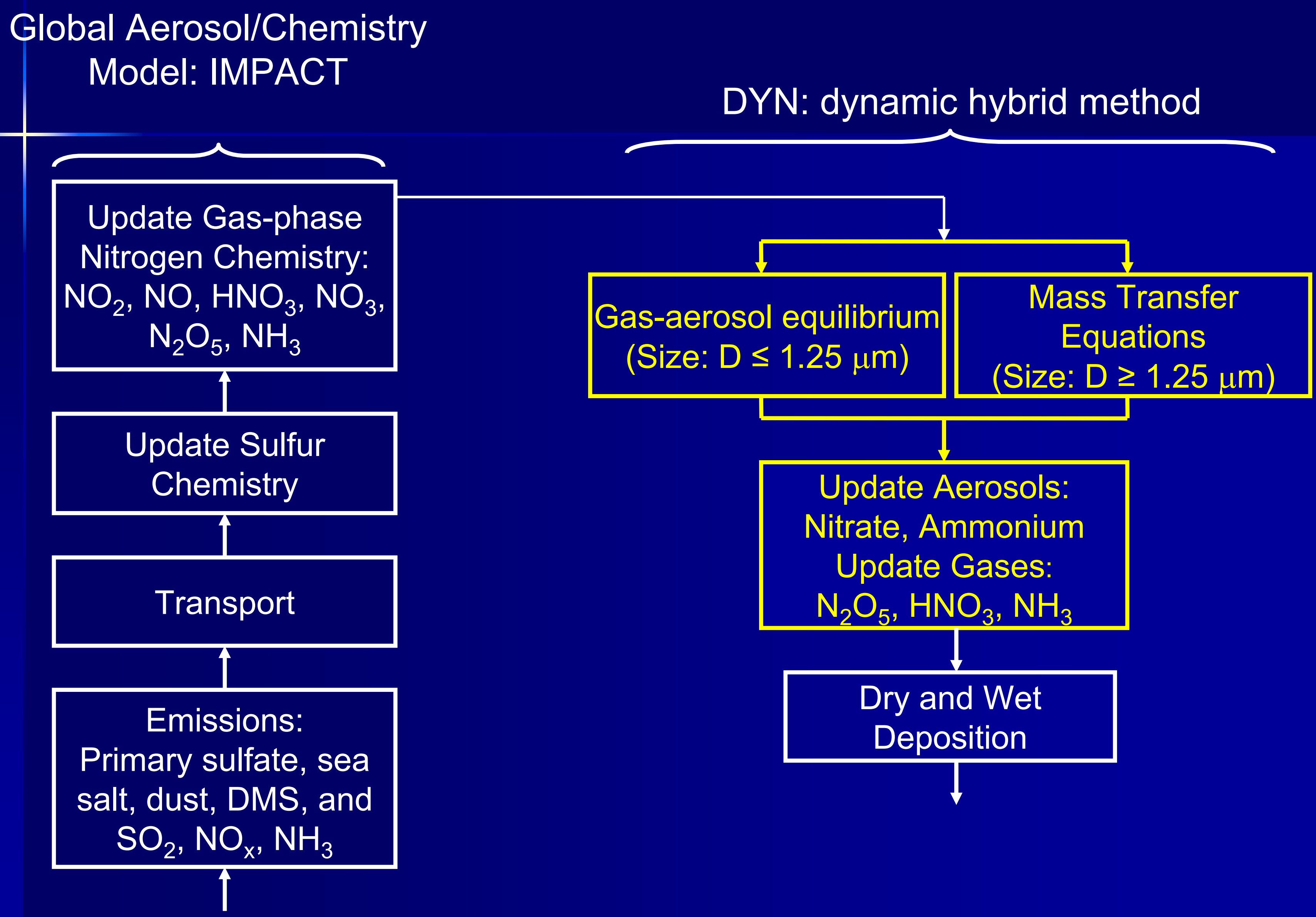
← C_i : aerosol concentration in size bin i

← Diffusion rate (*Fuchs and Sutugin*, 1971)

$C_{i,eq}$: equilibrium concentration on aerosol surface

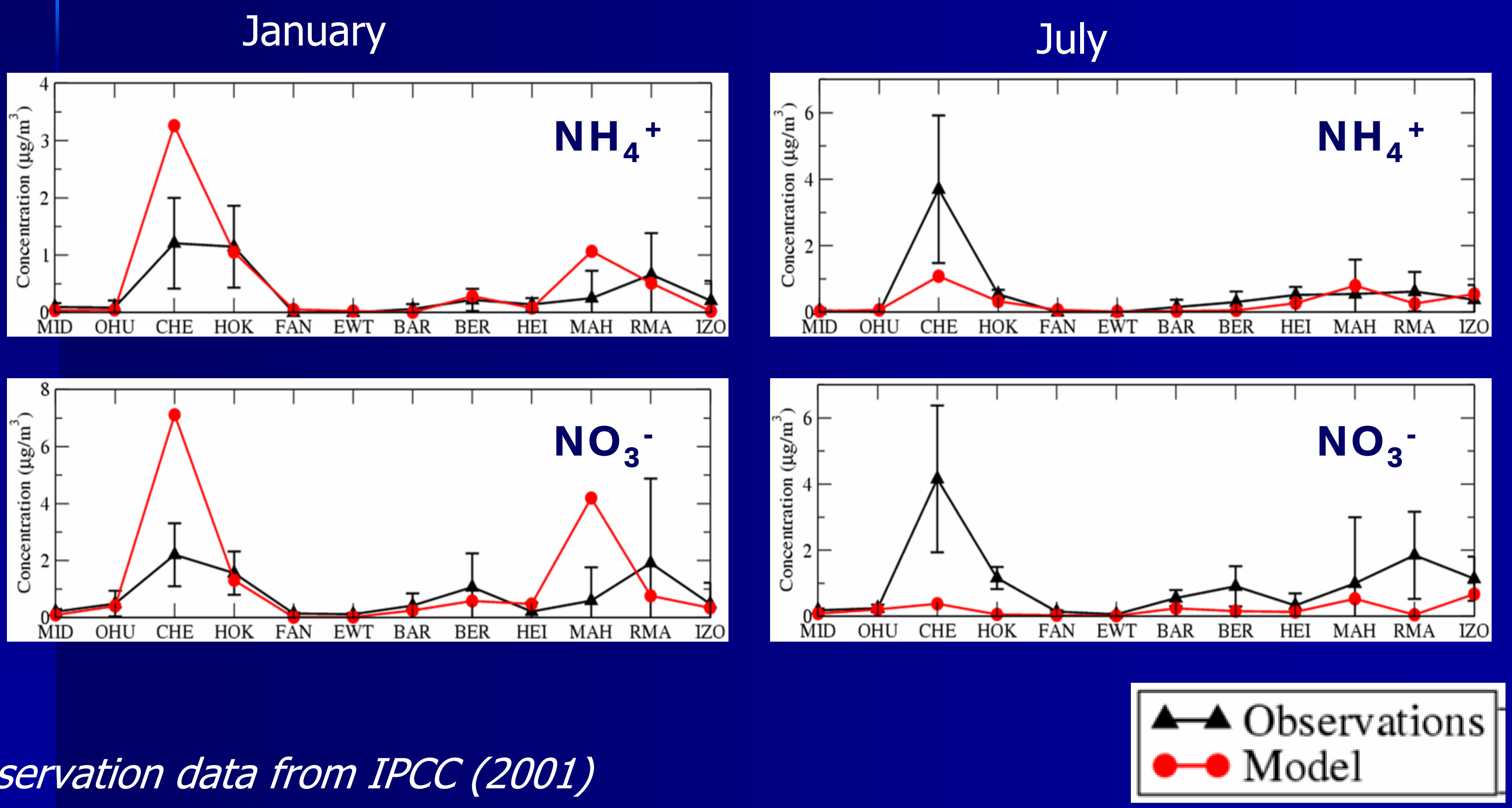
- determined by the aqueous-phase equilibrium;
- updated at an adaptive time interval, $\Delta t = 1/10 \times 1/\max(k_i)$

Integration to Global Aerosol Model



- The horizontal resolution of the model is 2° latitude by 2.5° longitude, with 26 vertical layers.
- The global aerosol/chemistry model was driven by DAO meteorological fields (1997-1998)
- Emission, transport and deposition modules were based on a global chemistry-transport model, LLNL/IMPACT (*Rotman et al.,* 2004).
- Sulfur chemistry, dust and sea salt aerosol modules were developed in the University of Michigan version of IMPACT (*Liu et al.,* 2005, J. Geophys. Res.).
- Nitrogen chemistry and ammonia cycle were described in *Feng and Penner* (2005, submitted).

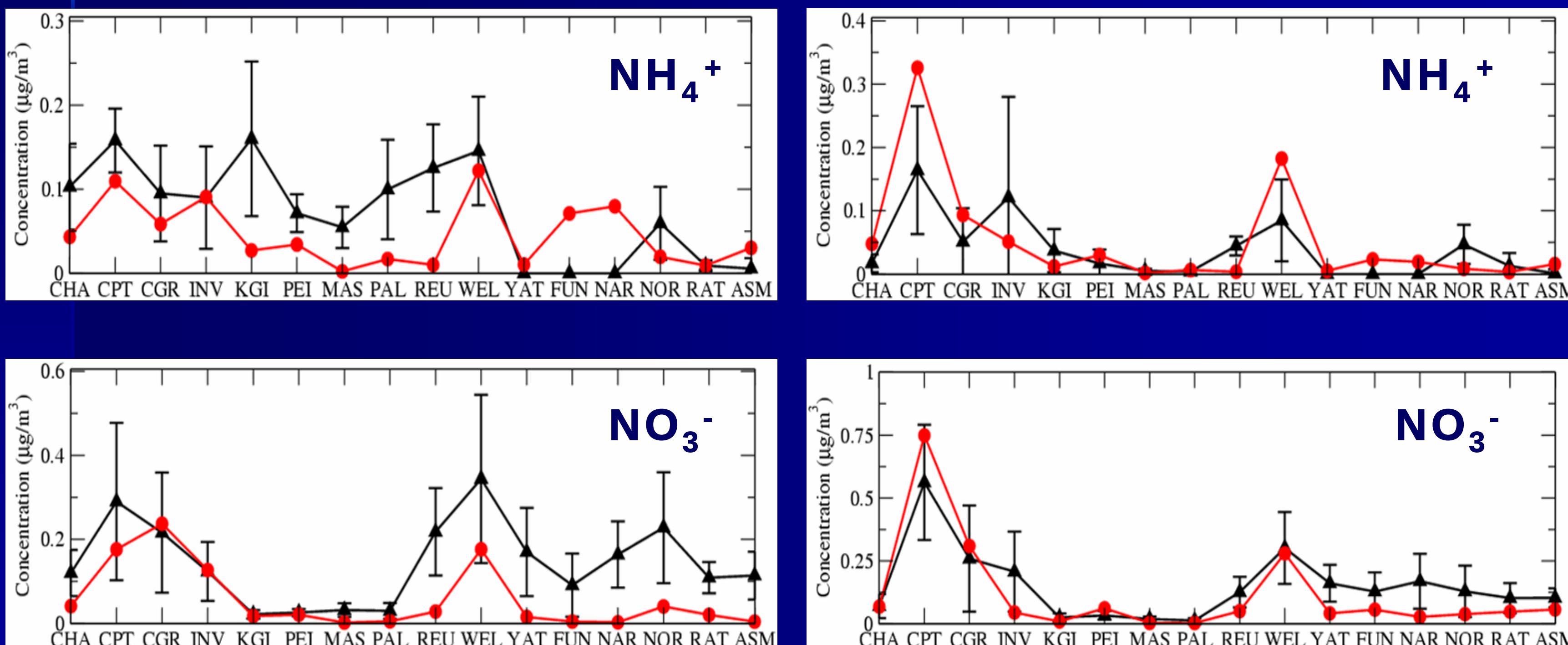
Modeled vs. Observed Surface Concentration at Marine Sites in the NH



Observation data from IPCC (2001)

Modeled vs. Observed Surface Concentration at Marine Sites in the SH

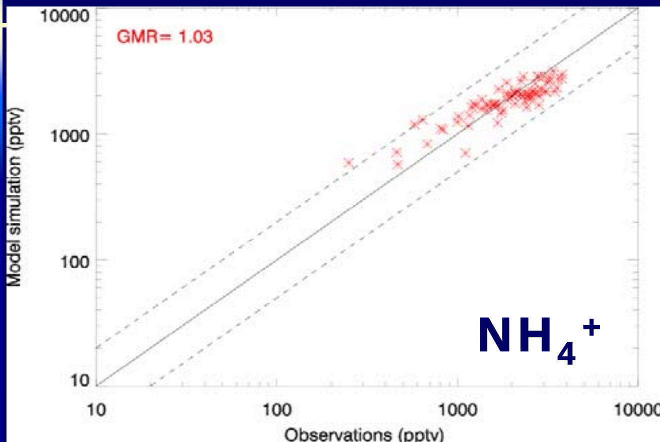
January July



Comparisons With Observations Over the Polluted Continents

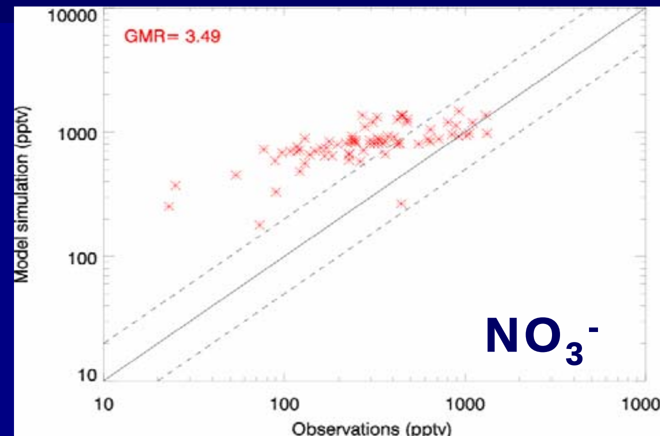
North America (EMEPS: 75 sites, 27°N-57°N, 65°W-107°W)

Model



Observation

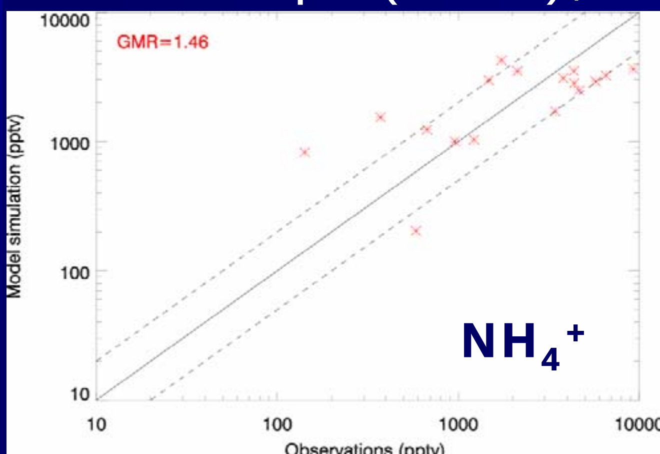
Model



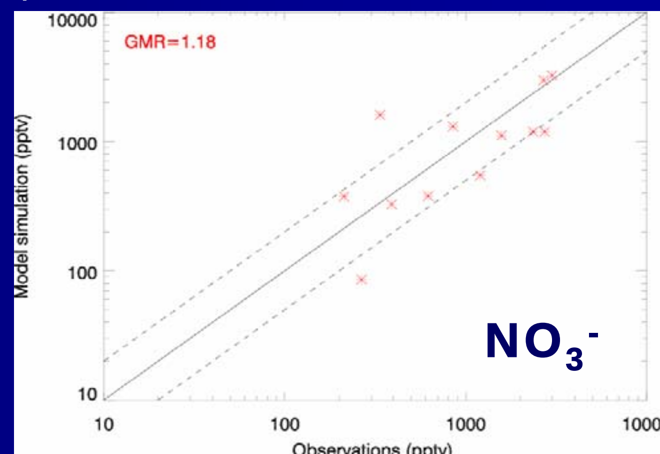
Observation

Europe (EMEF), 37°N-74°N, 29°E-21°W

Model



Model



Observation data from Adams et al. (1999)

Observation

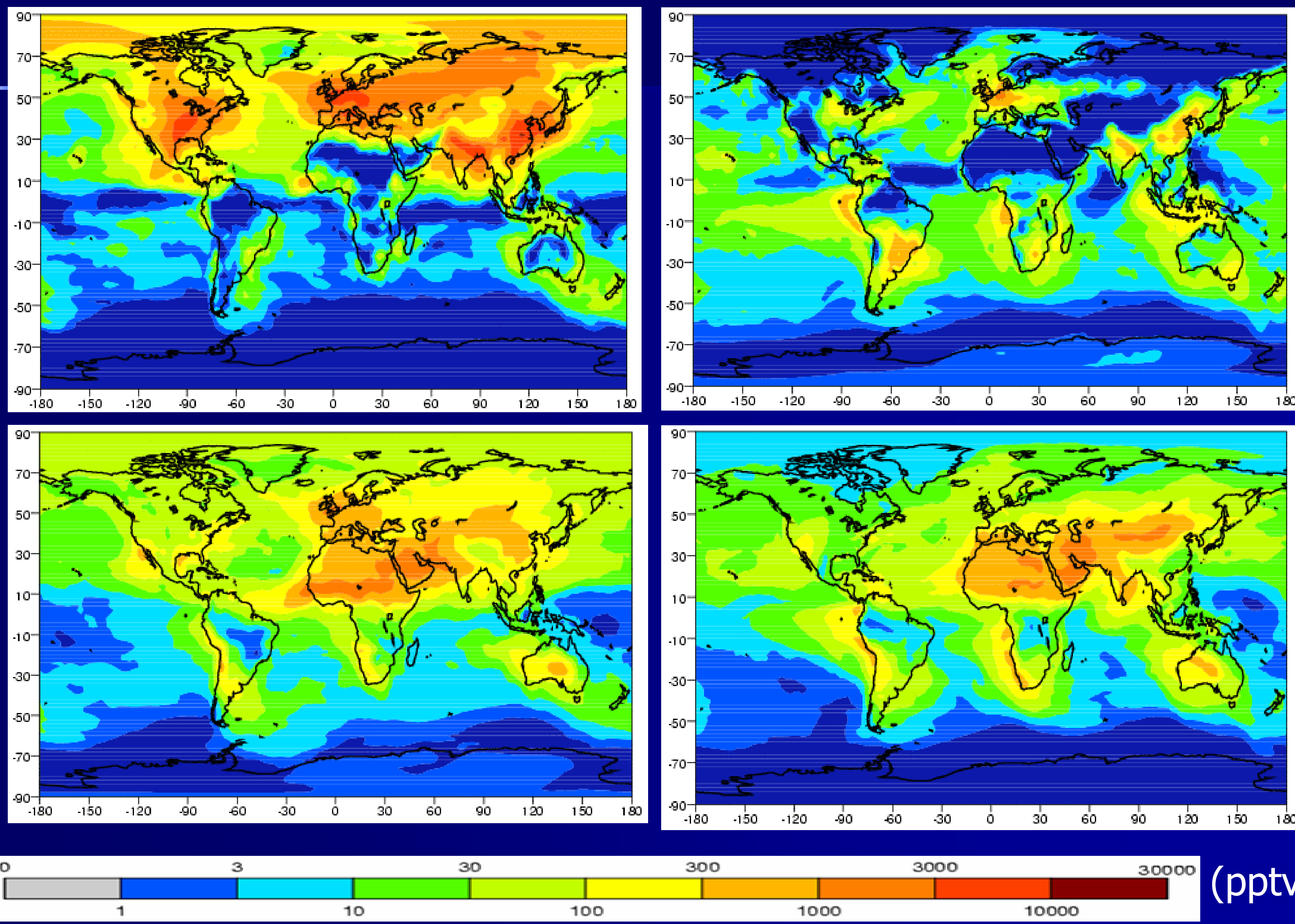
Nitrate Aerosol Surface Concentration (pptv)

January

July

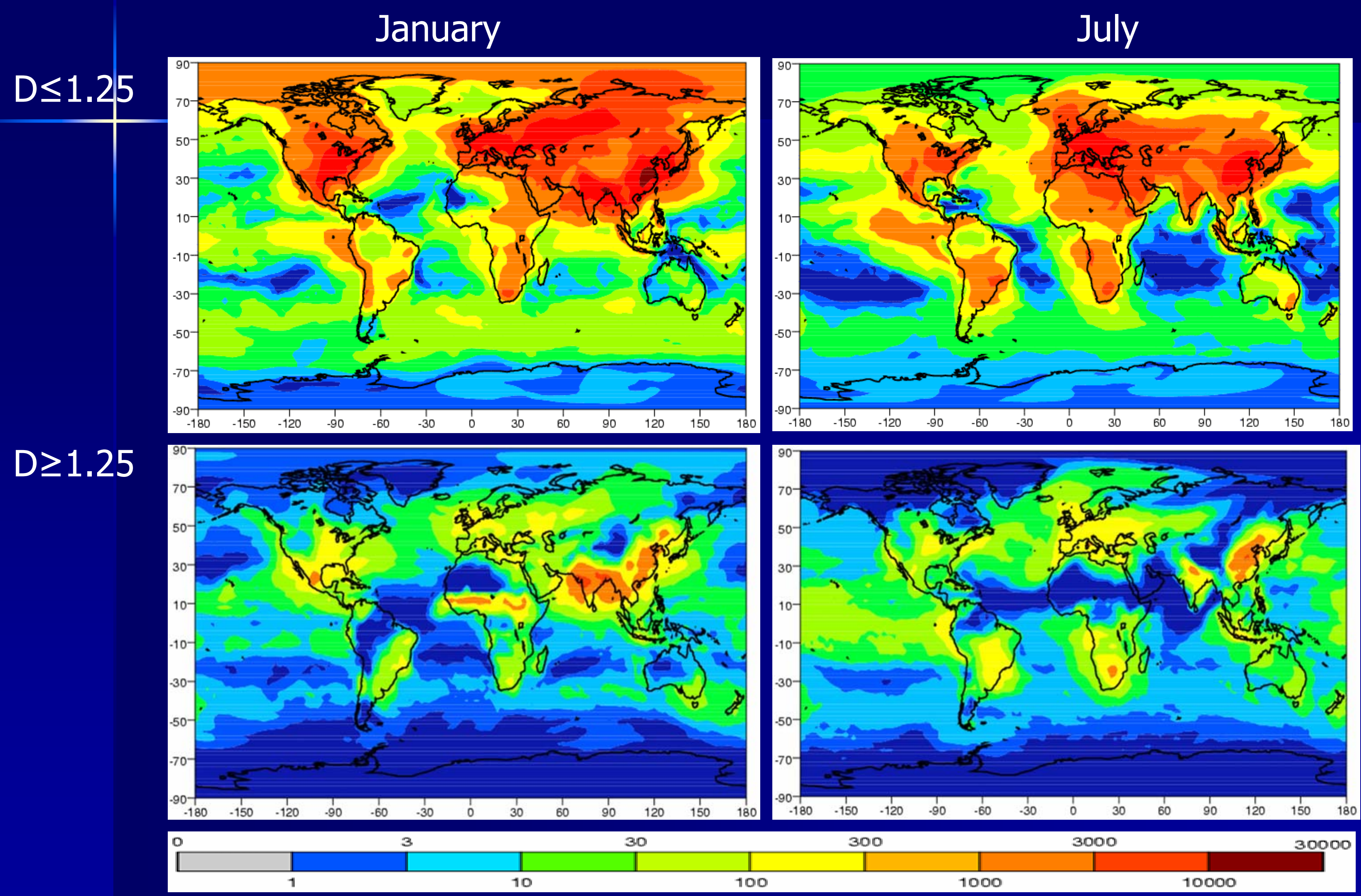
D≤1.25

D≥1.25

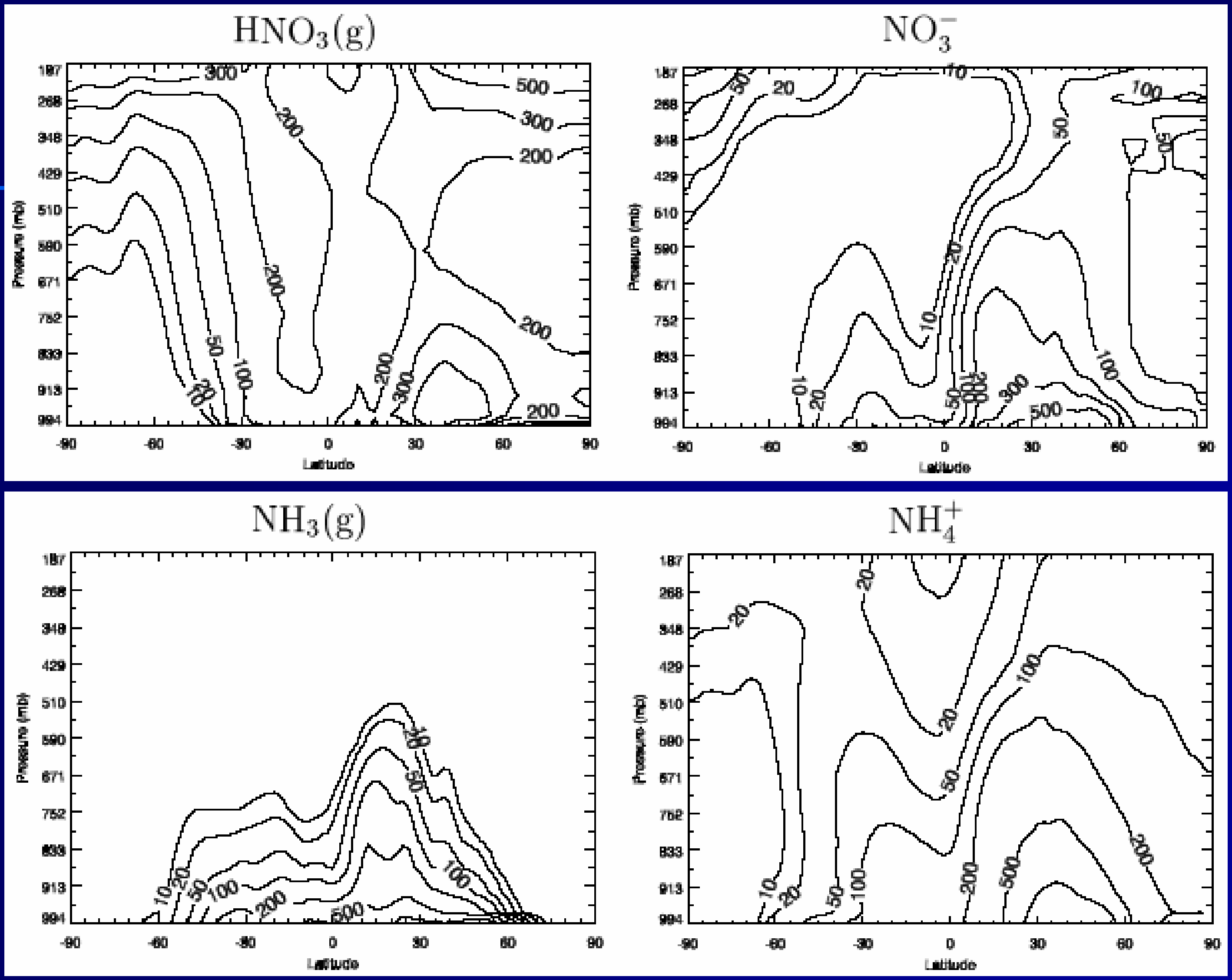


(pptv)

Ammonium Aerosol Surface Concentration (pptv)

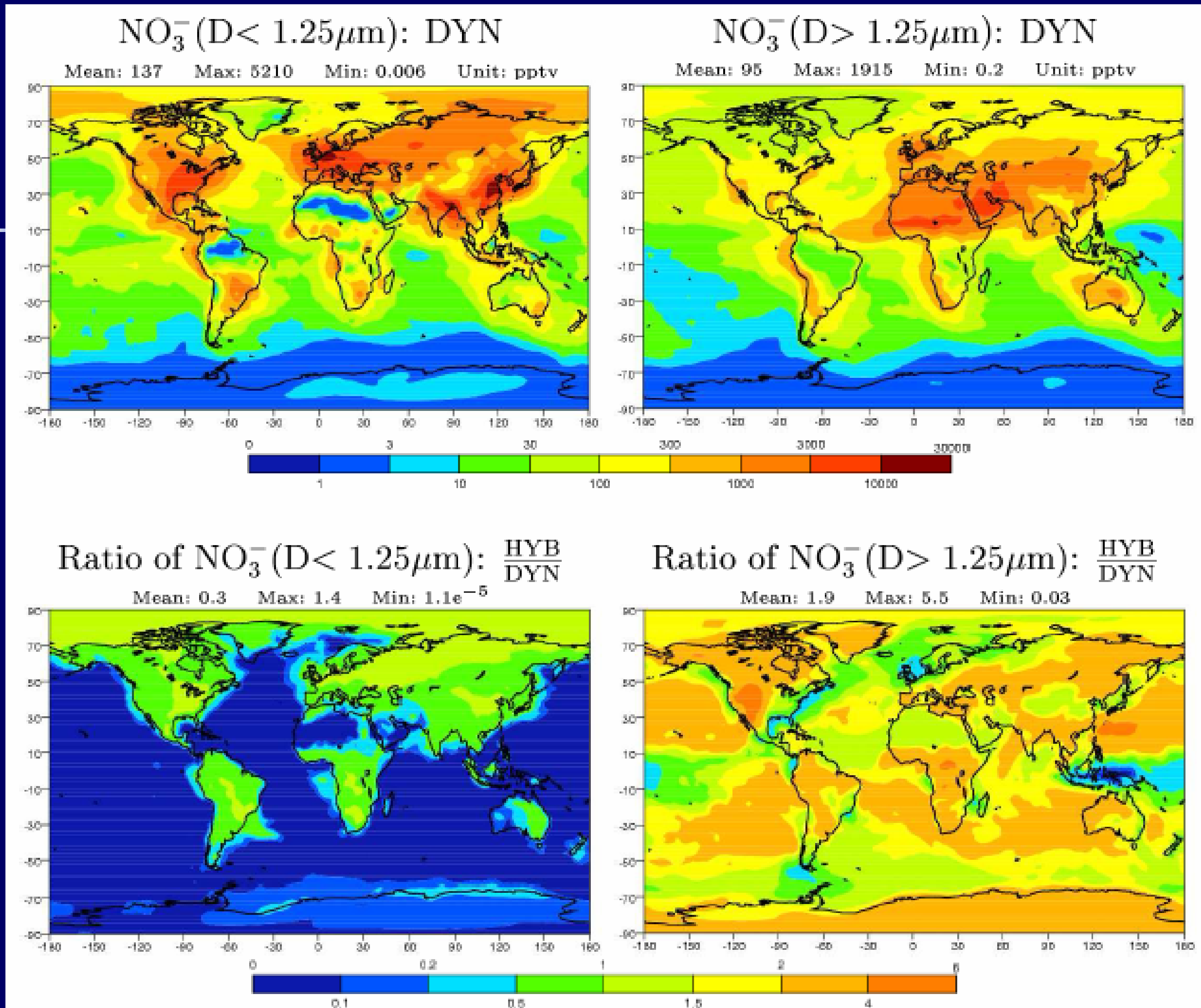


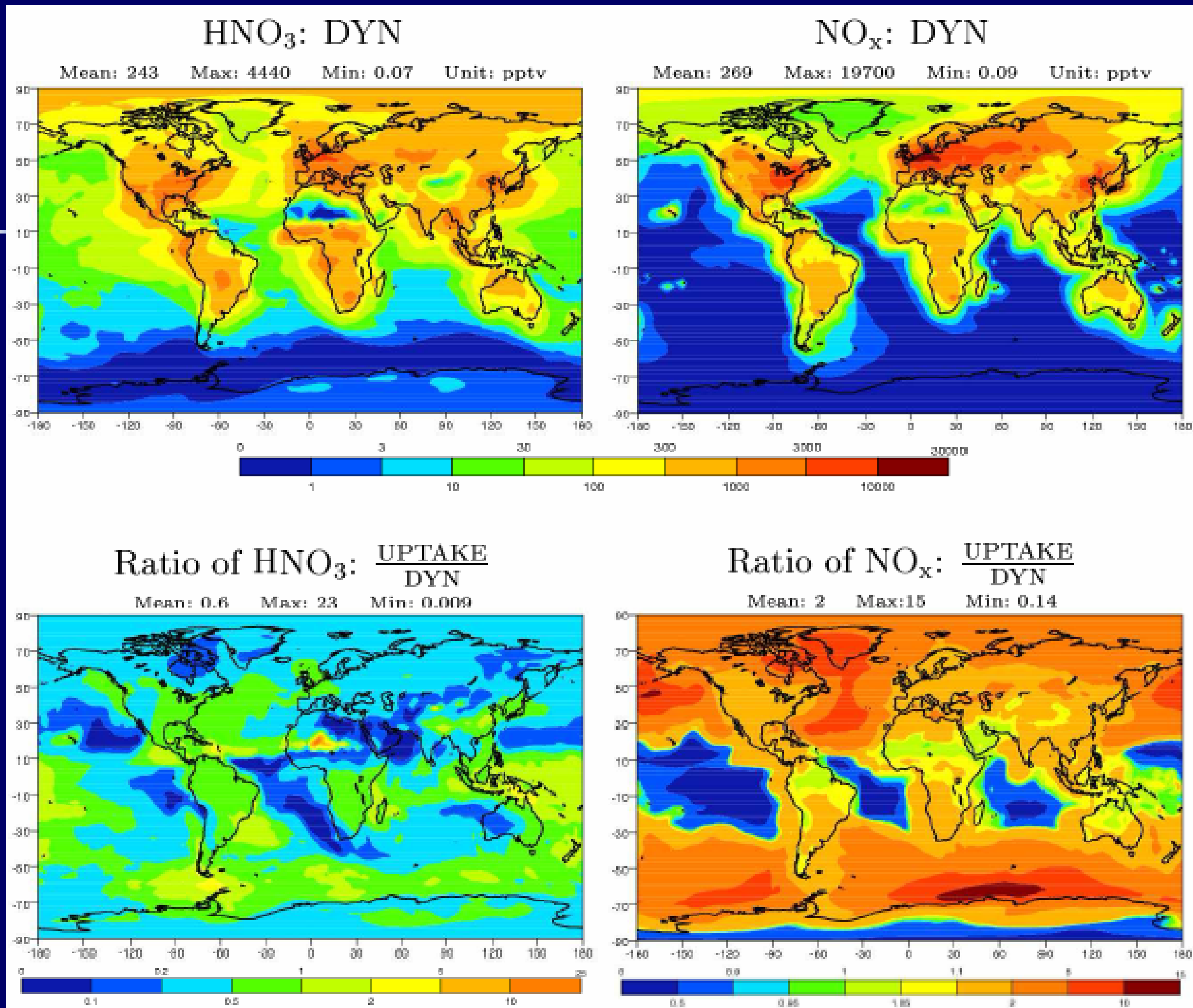
Units: pptv

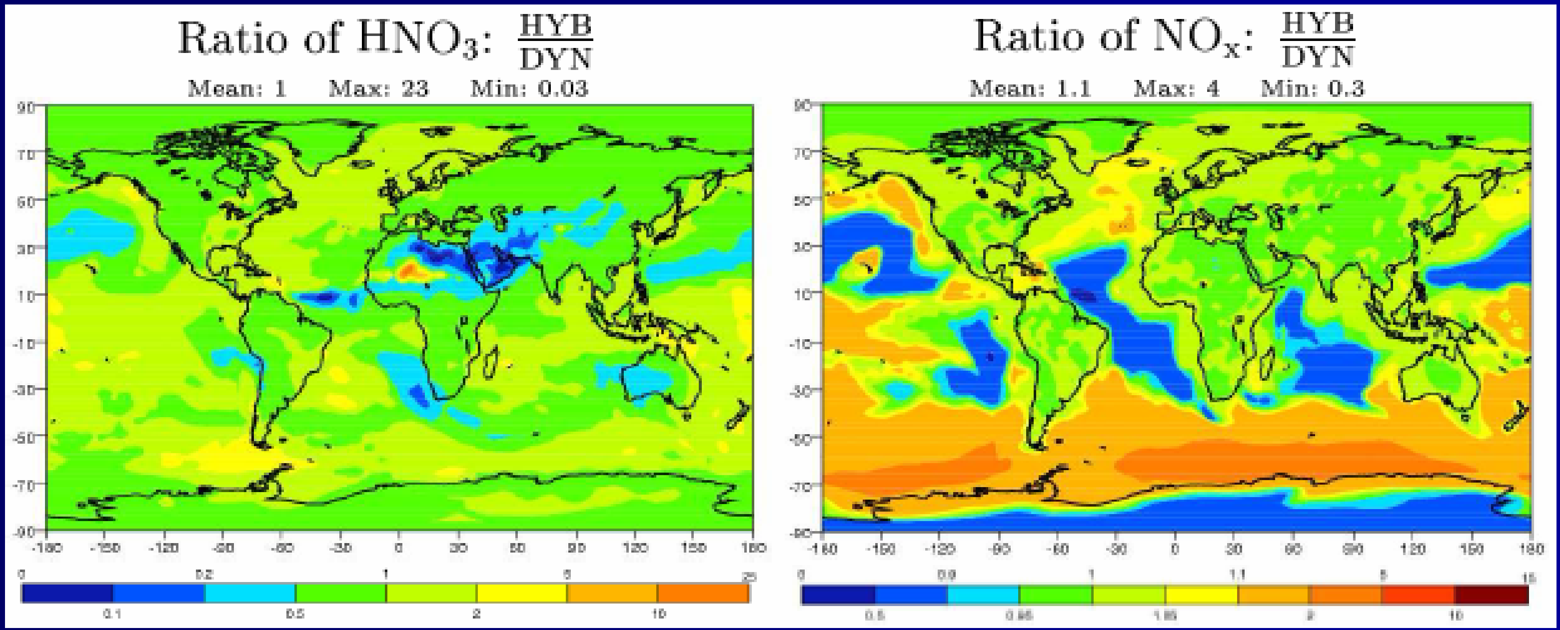


Pressure (hPa)

Latitude


NO_3^- (D< 1.25μm): DYN
Mean: 137 Max: 5210 Min: 0.006 Unit: pptv
NO_3^- (D> 1.25μm): DYN
Mean: 95 Max: 1915 Min: 0.2 Unit: pptv
0 3 30 300 3000 30000
1 10 100 1000 10000
Ratio of NO_3^- (D< 1.25μm): $\frac{HYB}{DYN}$
Mean: 0.3 Max: 1.4 Min: 1.1e^{-5}
Ratio of NO_3^- (D> 1.25μm): $\frac{HYB}{DYN}$
Mean: 1.9 Max: 5.5 Min: 0.03
0 0.2 1 2 6
0.1 0.5 1.5 4


HNO$_3$: DYN
Mean: 243 Max: 4440 Min: 0.07 Unit: pptv
NO$_x$: DYN
Mean: 269 Max: 19700 Min: 0.09 Unit: pptv
Ratio of HNO$_3$: $\frac{\text{UPTAKE}}{\text{DYN}}$
Mean: 0.6 Max: 23 Min: 0.009
Ratio of NO$_x$: $\frac{\text{UPTAKE}}{\text{DYN}}$
Mean: 2 Max:15 Min: 0.14



Ratio of HNO_3: $\frac{HYB}{DYN}$
Mean: 1 Max: 23 Min: 0.03
Ratio of NO_x: $\frac{HYB}{DYN}$
Mean: 1.1 Max: 4 Min: 0.3

HNO$_3$(g)

UPTAKE: 36%
HYBRID: 55%
DYN HYBRID: 70%

D<1.25μm

Fine-mode NO_3^-

UPTAKE: 24%
HYBRID: 13%
DYN HYBRID: 14%

D>1.25 μm

Coarse-mode NO_3^-

UPTAKE: 40%
HYBRID: 32%
DYN HYBRID: 16%

Overpredict super-micron nitrate aerosol

→ underpredict HNO$_3$(g)

⇢ underpredict NO$_x$ and O$_3$ ⇢ Underpredict/overpredict nitrate forcing?

Conclusions

- Nitrate aerosol burden is 0.16 TgN, with 43% in the sub-micron mode, and ammonium aerosol burden is 0.29 TgN (92%);
- EQ underestimates the sub-micron nitrate (10% of total HNO_3+NO_3^-) compared to DYN (13%);
- UPTAKE and HYB overpredict nitrate burden by 106% and 47% compared to DYN respectively, especially that in the super-micron mode;
- 68% of the heterogeneous conversion of N_2O_5 to nitrate (HNO_3 or NO_3^-) occurs on sulfate aerosol, with 30% and 2% on dust and sea salt, respectively. With sulfate excluded, UPTAKE overpredicts NO_x burden by 56% and surface NO_x concentration up to 5 times;
- HYB underpredicts surface sub-micron nitrate up to 50% over continents.

Global distribution and climate forcing of carbonaceous aerosols
Chung and Seinfeld, JGR, 2002

The global distribution of carbonaceous aerosols was simulated in the Goddard Institute for Space Studies General Circulation Model II-prime. Prognostic tracers include black carbon, primary organic aerosol, five groups of biogenic volatile organic compounds, and 14 semivolatile products of BVOC oxidation by O_3, OH, and NO_3, which condense to form secondary organic aerosols based on an equilibrium partitioning model and experimental observations.

The predicted global production of SOA is 11.2 Tg yr^{-1}, with 91% due to O_3 and OH oxidation.

Global distribution of secondary organic aerosols
Chung and Seinfeld, JGR, 2002

Classes of Reactive Terpenes used in the work

Class	*Composition*
I	α-pinene, β-pinene, sabinene, 3-carene, terpenoid ketones
II	limonene
III	α-terpinene, γ-terpinene, terpinolene
IV	myrcene, terpenoid alcohols, ocimene
V	sesquiterpenes

Terpenes are the only kind of hydrocarbons used on this work.

Aromatic species are not included, and aromatics do not contribute to the formation of SOA.

Global distribution and climate forcing of carbonaceous aerosols
Chung and Seinfeld, JGR, 2002

A parent hydrocarbon HC_i reacts in the gas phase with an oxidant OX_j (either OH, O_3, or NO_3) to form a set of products $G_{i,j,k}$, where $\alpha_{i,j,k}$ are mass-based stoichiometric coefficients.

$$HC_i + OX_j \rightarrow \alpha_{i,j,1} G_{i,j,1} + \alpha_{i,j,2} G_{i,j,2} + \ldots$$

$$[G]_{i,j,k} = \frac{[A]_{i,j,k}}{K_{om,i,j,k} M_o}$$

M_o is the concentration of total organic aerosol. $K_{om,i,j,k}$ is the equilibrium partition coefficient.

Global distribution and climate forcing of carbonaceous aerosols
Chung and Seinfeld, JGR, 2002

$$M_o = [POA] + \sum_{i,j,k} [A]_{i,j,k}$$

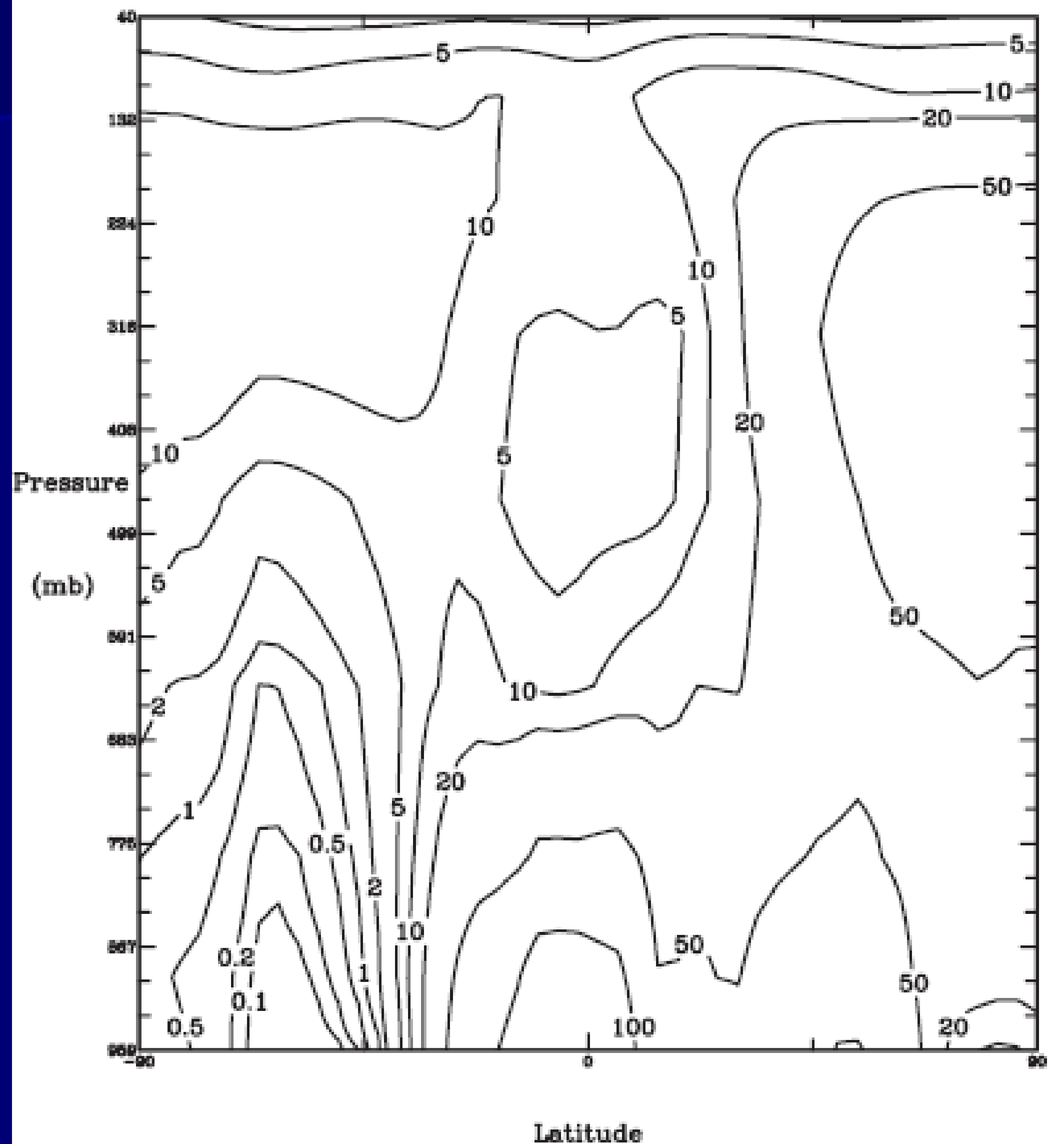
$$K_{om,i,j,k} = \frac{760\,RT}{10^6\,MW_o\,\zeta_{i,j,k}\,p^0_{L,i,j,k}}$$

$\zeta_{i,j,k}$ is the activity coefficient of compound $G_{i,j,k}$ in the organic aerosol phase, MW_o is the molecular weight of the organic aerosol phase, and $p^0{}_{L,i,j,k}$ (torr) is the vapor pressure of the compound at the temperature of interest (subcooled, if necessary).

$\zeta_{i,j,k}$ is assumed to be constant.

Global distribution and climate forcing of carbonaceous aerosols
Chung and Seinfeld, JGR, 2002

Predicted zonal annual average global SOA distribution (ng m^{-3}).



Current work

- The current work involves a similar approach to the Seinfeld one, but with the following modifications:

- Use of a more detailed chemical mechanism (189 chemical species and 611 chemical reactions).

- Inclusion of more organic species with potential to form SOA (aromatic acids, aromatic aldehydes and other similar species).

Current work

- Use of an updated emission inventory of black carbon, primary organic aerosol (FF POM: 3.06 Tg/yr; BB POM: 45 Tg/yr) and biogenic volatile organic compounds.

- The values for vapor pressure and activity coefficient of the new included organic species can be estimated based on data for similar molecules.